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LIST OF PATENTS AND PUBLICATIONS FOR APPLICANT'S INFORMATION DISCLOSURE STATEMENT	Applicant: Harvey A. Restaino et al.	
	Filing Date February 20, 2004	Group Art: 2838

U.S. PATENT DOCUMENTS

Examiner Initial		Document No.	Date	Name	Class	Sub Class	Filing Date If Appropriate
SB	BL	4,112,351	9/5/78	Back et al.	324	16	
	BM	4,114,083	9/12/78	Benham et al.	320	39	
	BN	4,126,874	11/21/78	Suzuki et al.	354	60	
	BO	4,178,546	12/11/79	Hulls et al.	324	158	
	BP	4,193,025	3/11/80	Frailing et al.	324	427	
	BQ	4,207,611	6/10/80	Gordon	364	580	
	BR	4,315,204	2/9/82	Sievers et al.	322	28	
	BS	4,316,185	2/16/82	Watrous et al.	340	636	
	BT	4,322,685	3/30/82	Frailing et al.	324	429	
	BU	4,363,407	12/14/82	Barkler et al.	209	3.3	
	BV	4,369,407	1/18/83	Korbell	324	416	
	BW	4,412,169	10/25/83	Dell'Orto	320	64	

FOREIGN PATENT DOCUMENTS

		Document No.	Date	Country	Class	Sub Class	Translation Yes No
SB	BX	03282276	12/12/91	Japan			Abstract Only
SB	BY	03274479	12/5/91	Japan			Abstract Only
SB	BZ	5216550	8/27/93	Japan			Abstract Only
SB	CA	59017894	1/30/84	Japan			Abstract Only

OTHER ART (Including Author, Title, Date, Pertinent Pages, Etc.)

	CB	"Internal Resistance: Harbinger of Capacity Loss in Starved Electrolyte Sealed Lead Acid Batteries, by Vaccaro, F.J. et al., AT&T Bell Laboratories, 1987 IEEE, Ch. 2477, pp. 128,131.

EXAMINER: 06/19/08	DATE CONSIDERED:

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INTERNAL RESISTANCE: HARBINGER OF CAPACITY LOSS IN STARVED ELECTROLYTE SEALED LEAD ACID BATTERIES

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Abstract

In many standby applications, the battery technology of choice is lead acid. Where the application is critical the state of health of the battery is a primary concern. A simple evaluation technique for determining the battery's performance would be highly desirable. Described are measurements of battery impedance made on a sealed lead acid battery of a particular type. At least one important failure mechanism, dryout, is usefully presaged by an increase in impedance of sealed lead acid batteries.The impedance rise, which is observed to be log-linear with time on float, is accompanied by a linear loss of cell weight due to water loss. The results suggest that battery impedance may provide a useful diagnostic for sealed lead acid batteries if simple calibration experiments are performed on cells of the type to be monitored.

Introduction

A cause for concern for many battery users, especially in critical applications involving uninterruptible power supplies, is the state of health of the battery. The user is particularly concerned with available Amp hrs., and , at the previous Intelec conference in Toronto, the question was asked on several occasions as to the best method(s) for evaluating battery performance while in service, and ultimately, how an indication of end of life is obtained. The obvious and most direct answer of course is a capacity discharge test. This solution however tends to be expensive, inconvenient and for the period of the test and subsequent recharge leaves the supported systems with little if any battery backup. The need therefore is for a procedure that minimally perturbs the system, is simple enough to be performed by the user as a periodic maintenance routine and ideally, is compatible with remote data collection techniques. Potentially interesting is the measurement of cell or battery impedance using a small amplitude A.C. At the high discharge rates employed in many U.P.S. systems the internal resistance becomes an important parameter in determining the available capacity of the cell or battery to a particular end voltage. The question, however, is whether impedance measured using A.C. can function as a reliable performance indicator, where performance is defined as available capacity (Amp hrs.) under a large D.C. load. DeBardelaben [1] reported cell impedance measurements on 7000 Amp hr lead antimony telephone cells and concluded that impedance measurements could substitute for discharge testing. The main focus of that work, however, was the measurement technique itself, primarily the problems associated with obtaining meaningful data while the battery remained in service. There was very little discussion of the physical significance of the impedance measurement in terms of the reactions occurring in the battery nor any mention of the statistical significance of the measurement and its robustness as a general measurement tool. This report describes experiments on a particular starved electrolyte sealed lead acid battery with emphasis on the validity and reliability of the measurement and the mechanism of failure.

Experimental

The lead acid batteries used in this study were the starved electrolyte "sealed" (valve regulated) type, rectangular in shape with an advertized capacity of 38 Ah at the 20 hour rate. The batteries were manufactured and tested as six cell (12V) modules. The "as received" (from the manufacturer) batteries were initially given two discharge-recharge cycles. The discharge load was a constant current of 96 Amps, which is a particular U.P.S. maximum average load current. Recharge to 120% of the discharge capacity was accomplished at the recommended float voltage of 13.62 volts per battery. The two cycle exercise provided "as received" capacity data plus a battery to battery comparison. Battery weights were measured using a Mettler PS 15 balance of 1 gm. accuracy. Battery impedance measurements were made with a Keithley Model #503 A.C. resistance bridge at 40 Hz frequency. Comparative measurements at 1 KHz were accomplished with a Hewlett Packard Milliohmeter model #4328A. Three test temperatures 20°C, 40°C and 50°C, controlled to + 1°C by the use of environmental chambers were chosen as potentially representative of actual application conditions. At each test condition, six 12V modules were connected in parallel and floated at 13.62V per battery. The current to each module was monitored using current measuring resistors.

Impedance and phase angle spectra were measured using a Hewlett Packard 4129A Impedance analyzer. The spectra of a fully charged battery are shown in Figure 1. The region

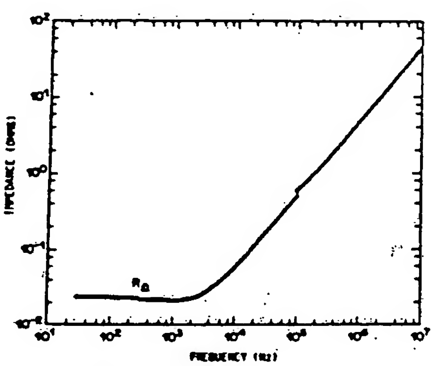

Figure 1. Frequency-Impedance Spectra.

of interest in this case occurs below 2KHz where the impedance is independent of frequency showing its major component to be resistance. Measurements performed at 40Hz show this resistive region to extend to at least that frequency. At the frequencies used in these experiments therefore (40Hz and 1KHz) the measurement of impedance provides a true resistance unencumbered by the inductive reactance that appears above 2KHz.

Results and Discussion

Prior to any impedance measurements each battery was given the two initial cycles described previously. A discharge curve typical of that obtained from the second initial cycle is shown in Figure 2. For a sample of thirty batteries discharged at an ambient temperature of 25C the average duration of the 96A discharge was 6.8 + 0.4 minutes to an end voltage of 10.5 volts.

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At such high discharge rates there is no significant plateau portion to the curve, which decays almost linearly with time. In a typical U.P.S. the end of a discharge is generally defined by an end voltage; for example, 10.5V for a nominally 12V battery. A relatively steep linear decay as described by Figure 2 means that the end voltage specification has a significant effect on the amount of capacity available. The average float currents demanded by these batteries at the various test temperatures are shown in Figure 3. They

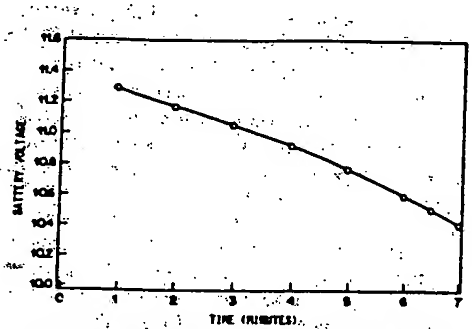

Figure 2. As Received Battery Discharge Curve at 25°C and 96 Ampere Load

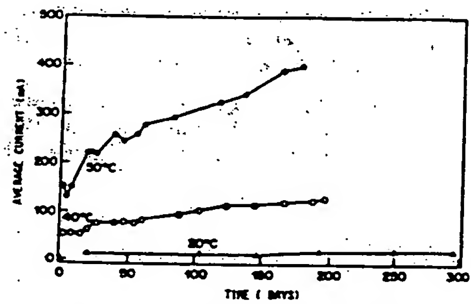

Figure 3. Battery Float Current at Various Temperatures

increase with time in a gradual fashion. No evidence of a thermal current runaway, as evidenced by an exponential rise in current with time, was observed in any of these experiments. At intervals during the experiment, the batteries were discharged at the temperature of the experiment using a constant current load of 96 Amps. The discharge capacities thus obtained are given in Figure 4. The effect of ambient

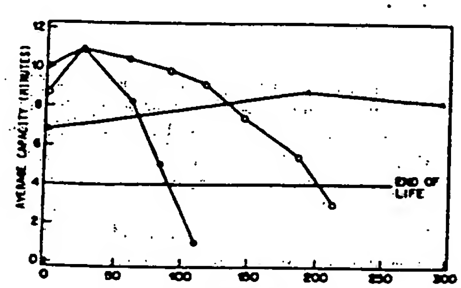

Figure 4. Capacity Degradation at Various Test Temperatures

temperature on battery life is illustrated. End of life, application defined as the point at which the battery could not sustain a voltage of greater than 10.5V for a period of greater than 4 minutes, would be 99 days @ 50°C and 204 days @ 40°C. This contrasts with batteries on test at 20°C, for which current test data indicate a life in excess of 600 days. This rather better performance at 20°C cannot be relied upon, however, because U.P.S. gear is conventionally employed to power equipment that is designed to operate at temperatures up to 40°C [2]. Battery ambients between 40°C and 50°C are thus to be anticipated as possible in some U.P.S. applications. The relatively short lifetimes of this particular battery under these conditions illustrate the concern of the U.P.S. owner and highlight the need for a reliable, simple measure of battery capacity.

Figure 5 contains a family of discharge curves that illustrate the effects of time on test at 40°C. As the battery aged, the

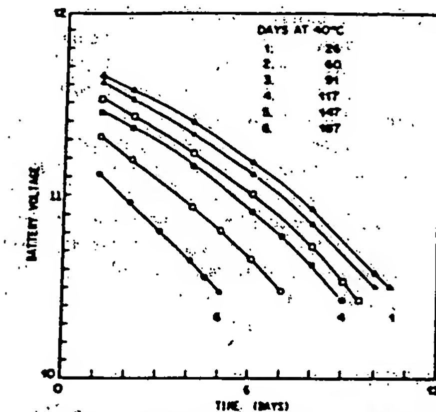

Figure 5. Effect of 40°C Operation on Discharge Capacity

absolute value of the voltage at a particular time during the discharge was lowered. It is interesting to note the almost parallel relationship of the discharge curves. The effect on the capacity of this lowering of discharge voltage is obvious. The difference between the voltage at the beginning of the discharge and the end voltage becomes smaller, while the rate of voltage decay remains constant, thus reducing the time to reach the end voltage. This behavior is highly suggestive of an increase in battery internal resistance. The measured impedance increase that accompanies aging for 117 days @ 40°C (curve 4) for example is 2.2mΩ. If this were the absolute value of the battery internal resistance (simply Ohms law) then it would result in a 210 mV drop in plateau voltage for a discharge current of 96 amperes. The experimental value of 250 mV is in reasonably good agreement although it obviously does not tell the whole story. As the cell impedance further increases this simple Ohms law relationship becomes less valid. The values of the actual plateau voltage decrease become proportionately much larger than that calculated from the product of the impedance increase and discharge current as aging progresses. A number of mechanisms might be responsible for this increase, but their identification will require further study. All the resistance vs time data for the 38 Ah battery are plotted in Figure 6. That the log of the resistance varies linearly with time is shown, and this data, together with that from Figure 4 (capacity as a function of time) indicate that at

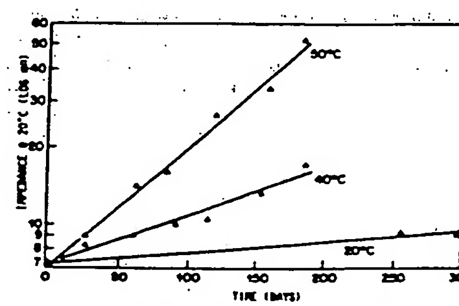

Figure 6. Battery Impedance Increase at Test Temperature

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the defined end of life (4 min to 10.5V) the measured impedance has approximately doubled, from 7mΩ to 19mΩ at 40°C and 17mΩ at 50°C, from its as received (new) value for both the 40°C and 50°C experiments. Interestingly therefore, separate batteries brought to the same defined end of life by different experimental conditions had similar impedances at end of life. Further evidence of the relationship between measured impedance and available capacity is provided in Figure 7 where they are plotted

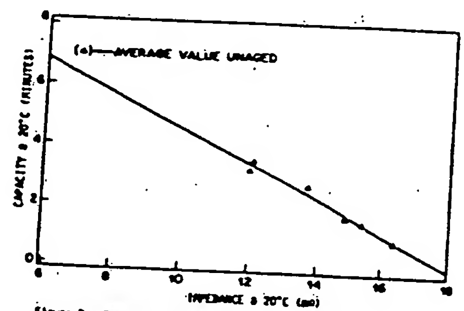

Figure 7. Capacity - Impedance Relationship After 50°C Aging For 62 Days

versus one another. Although these data were obtained from batteries on test for 62 days at 50°C and 13.62V, or 2.27V per cell, the relationship was found to be true for all the experiments. The excellent correlation between available capacity and measured impedance means that it should be possible to accurately predict the available capacity from a measurement of the battery impedance; a finding that might be extrapolated to new as well as aged batteries.

To further test the validity of this idea, two sets of batteries other than those of the present experiment were obtained. The first set were 15 Ah -12V batteries of the same type (manufacturer's designation) as the 38 Ah -12V batteries described previously. These particular batteries had been part of a room temperature float experiment, having been on float @ 13.62V per battery and 23°C for varying times up to two years. A typical UPS discharge load for this particular battery size would result in a discharge current of 48 amps and this value was selected as the discharge current in the subsequent test of the batteries. These particular batteries had widely differing discharge characteristics and hence were considered suitable for testing the hypothesized relationship between impedance and capacity. They also represented a variety of manufacturing lots over a two-year period. This, therefore, was a reasonably robust test in that it contained a representative example of this particular product. Impedance was measured with the Hewlett Packard milliohmeter (1000Hz) and plotted against discharge time to 10.5V for a discharge current of 48 Amp. The results, given in Figure 8, confirm the linear relationship between capacity and impedance. Given the defined end point of four minutes discharge duration it is apparent from Figure 8 that batteries

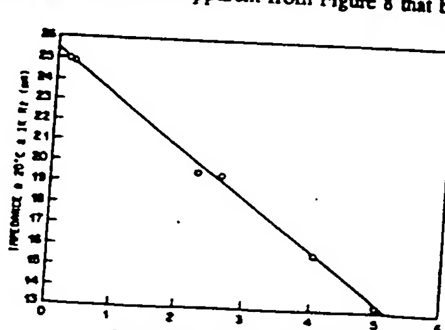

Figure 8. Capacity-Impedance Relationship After Aging at 23°C

with impedances of greater than 16mΩ, measured at 20°C and 1KHz, are unacceptable. Furthermore, impedance measurements of greater than 25mΩ indicate a battery with no capacity whatsoever to an end voltage of 10.5V. Figure 8 in essence can be used as a calibration curve for this particular 15 Amp per hour battery. The second set of batteries was interesting from two standpoints. First, the batteries were taken from an actual U.P.S. that had been operating in its designed environment and second, the batteries tested were near end of life. The batteries were connected into a 120V string that was designed to discharge at a 48 Ampere maximum rate. Because the discharge curves at this rate are very nearly linear, a plot of battery voltage at fixed time is an equally effective measure of capacity as is time at fixed voltage. Battery voltages at the 30 second discharge points are thus plotted against resistance in Figure 9, where once again, a linear relationship is evident.

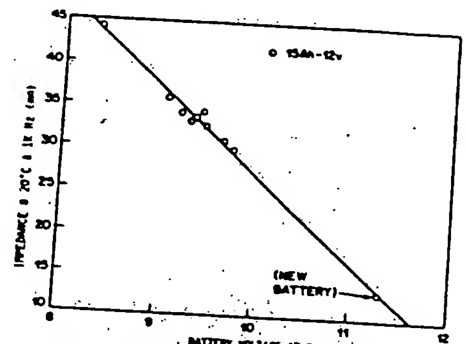

Figure 9. Capacity-Impedance Relationship of Field Aged Cells

The data from Figure 8 would suggest that any battery with a measured impedance of greater than 25mΩ would have minimal capacity to a 10.5V end voltage. The data of Figure 9 fully concur. All the batteries had measured impedances of greater than 30mΩ, and 30 seconds into the 48 Amp discharge all the batteries were below 10 V. Once again the linear relationship was observed. Particularly satisfying was the apparent sensitivity of the measurement. It was possible to determine fairly subtle variations in capacity using this measurement and also to cover the entire range of battery life.

Although these results must be considered preliminary and as yet have only been applied to one family of product, there does appear to be promise for the measured impedance to be a useful indicator of capacity in specific applications.

Included as a measured parameter in the laboratory experiments was the weight of the battery. Expressed in Figure 10 as weight loss and plotted versus time on test, it shows the batteries at each test condition to be losing weight at a rate proportional to the test temperature and linear in time. This weight loss is considered to be primarily due to the loss of water from the battery. Experiments performed to

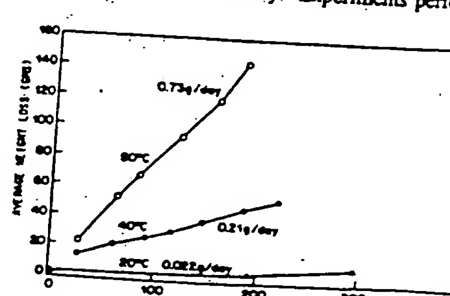

Figure 10. Battery Weight Loss at Test Temperature

measure the gas evolution rates as well as an analysis of the gas composition revealed that only approximately 10% of the weight loss could be attributed to actual electrolysis of water. In an attempt to identify the major cause of the water loss, a semi logarithmic plot was made of the water loss rate vs the reciprocal of the absolute temperature. It is shown in Figure 11. Results from the three test temperatures fall on a straight

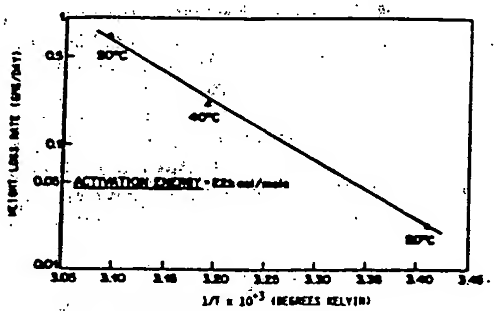

Figure 11. Water Loss Rate at Test Temperature

line, the slope of which implies an activation energy of 22kcal/mole, were the process described attributed to a single, thermally activated process. However water loss in this case is not attributed to any known single mechanism. In fact, it is believed that water loss from the batteries is most likely the result of the interaction of several mechanisms including evaporation, diffusion through the case material and electrolysis. Analysis of the separator material at end of life revealed that approximately 8% of the water initially present was lost. The effect of replacing this lost water is shown in Figure 12. The two batteries represented

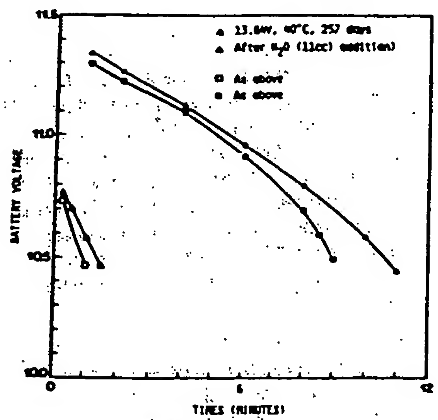

Figure 12. Replacement of Lost Water

had been on float at 13.62V per battery and 40°C for 257 days. The discharge current in this experiment was reduced from 96 Amps to 70 Amps to increase the sensitivity of the experiment since little capacity remained at 96 amperes. The discharges were run at 23°C. Each battery had lost 66 gms during the experiment and following the above discharges, this amount of water was replaced by adding 11 gms of water to each cell. The effects of the water additions are apparent. Given an end voltage of 10.5V the discharge time increased from approximately one minutes to approximately 10-11 minutes. A new battery would typically provide a discharge time of approximately 14 minutes. That water loss played a major role in determining the life of these particular batteries therefore was clear. Earlier a strong correlation was identified between available capacity and measured battery impedance. A major factor in determining available capacity has now been shown to be the amount of water in the battery. Since the battery operates in a starved electrolyte condition it perhaps is not surprising that small water losses can result in a breakdown of electrolyte continuity that increase the internal resistance.

Certainly the small amounts of water involved would not seriously effect the conductivity of the sulphuric acid solution itself. However, even though the precise mechanism is presently unclear, what is clear is that there appears to be an extremely strong correlation between measured impedance and battery performance that perhaps portends hope for a state of health indicator.

Conclusions

A strong correlation between measured impedance using commercially available resistance meters and battery performance has been demonstrated for a particular battery type. At 40°C and 50°C the major cause of capacity loss in this battery type is the loss of water from the battery. At high rates of discharge small losses of water (8%) can dramatically effect battery performance.

References

[1] S. DeBardelaben, Intelec 86 Toronto, Canada, Page 365.

[2] See for example AT&T 3B2/310 Computer Owner/Operator Manual.